The Critical Constants and Orthobaric Densities of Xenon.

By HUBERT SUTTON PATTERSON, B.SC., RICHARD STAFFORD CRIPPS and ROBERT WHYTLAW-GRAY.

Rudorf, in a paper on the rare gases and the equation of state,[*] has drawn attention to the high value found by Ramsay and Travers for the density of liquid xenon at its boiling point.[†] As is well known the atomic volume in any group of elements in the periodic table either increases regularly with rise of atomic weight or remains approximately constant, so that it is to be expected that the atomic volume of xenon would be greater than that of krypton, since the value for krypton exceeds that of argon.

If Rudorf's calculated value for the density of neon is taken into account, this anomaly becomes more striking, as is shown from the following table taken from his paper :—

	Neon.	Argon.	Krypton.	Xenon.
Density	1·24	1·404	2·196	3·58
Atomic volume	16·1	28·4	37·8	36·6

According to Rudorf the density of xenon near its boiling point should be 2·68, which would lead to an atomic volume of 48·8, but this question can only be settled by fresh experimental evidence.

For other reasons a study of the densities of liquid xenon and its saturated vapour appeared to us of interest, for the critical volume of this substance has never been determined, and at the commencement of this work the validity of Cailletet and Mathias's law of rectilinear diameters had never been tested with any of the argon series of gases. It might be expected that these gases on account of the simple structure and non-valent character of their molecules would approximate closely in behaviour to the requirements of the kinetic theory of gases and would follow the equation of van der Waals. This equation gives for the ratio of critical density to theoretical density at critical point the value 2·667, and D. Berthelot has calculated[‡] from Ramsay and Travers' densities of liquefied argon that the ratio for this

[*] 'Ann. des Phys.,' 1909, vol. 29, p. 751.
[†] 'Phil. Trans.,' 1901, A, vol. 197, p. 74.
[‡] 'Journ. de Phys.,' III, 1901, vol. 10, p. 611.

element lies between 2·62 and 2·71.   Rudorf, however, by the use of the data of Baly and Donnan for the liquid densities* deduced the value 2·95, which, although slightly greater than the theoretical, is much lower than the corresponding value for gases such as CO_2, N_2O, SO_2, which possess a ratio approximating to 3·6.   Sydney Young† has shown that for a large number of organic liquids this ratio is nearly constant and differs only slightly from 3·77, and regards this number as characteristic of normal non-associated substances.   If, however, it should prove that this ratio for the monatomic gases is markedly lower than that for polyatomic gases and vapours, an interesting light would be thrown on the question of molecular association in the liquid state and it would lend support to the view which has often been expressed that all normal liquids are partially associated.

These considerations made us anxious to revise the critical constants of xenon and to determine its orthobaric densities; and the kindness of Sir William Ramsay in willingly placing at our disposal the whole of his stock of this very precious gas has enabled us to carry out the measurements with highly purified material and with quantities sufficient to ensure a fair degree of accuracy in the results.

Experimental.—The original determinations of the density and critical constants were carried out by Ramsay and Travers with only about 3 c.c. of gas measured at normal temperature and pressure, and this quantity when liquefied yielded a volume of liquid in the neighbourhood of its boiling point of only 6 cu. mm.

In consequence the xenon could not be effectively purified by fractionation and in their paper the authors claim for their measurements no high degree of accuracy.   The specimen of gas investigated by us was originally obtained by Ramsay and Moore‡ from the residues of about 120 tons of liquid air presented to them by M. Claude, of Paris.   The gas after careful fractionation was employed by Moore§ in the determination of the exact atomic weight of xenon.   The xenon, which was of a volume of about 120 c.c. at normal temperature and pressure, was, when it came into our hands, in a high state of purity, but in order to obtain a specimen completely free from possible traces of krypton and air, the whole amount was first solidified in a bulb of small volume and a small amount of uncondensable gas which was present was removed by means of a mercury pump.   The remaining gas was surrounded by a bath of cooled pentane,

---

* 'Journ. Chem. Soc.,' 1902, vol. 81, p. 907.
† 'Phil. Mag.,' 1900.
‡ 'Roy. Soc. Proc.,' 1908, vol. 81, p. 195.
§ 'Trans. Chem. Soc.,' 1908, vol. 93, p. 2182.

the liquid xenon allowed to boil away, and the last fraction, consisting of about 20 c.c., was collected for these measurements. The densities of liquid and vapour were measured in a graduated capillary tube A of approximately 1 mm. internal diameter closed at one end and sealed at the other on to a wider tube B which served as a reservoir for the gas.

The capillary carried a nut C by means of which the tube could be screwed into position on a modified Andrews apparatus. The capillary was very carefully calibrated by means of mercury before it was sealed up and the end where the readings of the liquid were taken was specially studied. The form of the tube and the method of filling is best followed from the diagram.

The solid xenon, contained in a small fractionating vessel (not shown), was allowed to flow into the perfectly dry and air-free experimental tube AB and was re-condensed again, thus washing out the calibrated tube and its connections. This washing was repeated many times before each filling.

In order to fill the tube, the end A was cooled by immersion in liquid air until sufficient xenon had solidified in it, and a very complete exhaustion was then carried out with the Töpler pump. At the end of this operation, the solid xenon in the capillary was allowed to liquefy and some allowed to boil away into the pump, whence it could afterwards be collected. Finally, A was again cooled, the reservoir B completely filled with

FIG. 1.

mercury to a point E on the capillary, and the mercury thread was frozen by surrounding the tube below E with a paper vessel filled with solid CO_2. The nut and experimental tube were then disconnected at the rubber connection D from the rest of the apparatus and transferred to the compression apparatus. We found all these precautions were absolutely necessary in order to fill the tube with gas which should afterwards liquefy
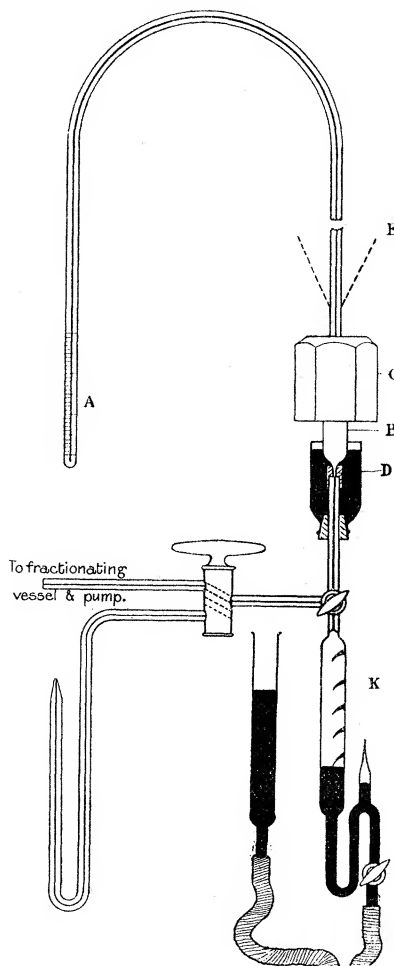
completely at constant pressure. After the measurements of density had been made, the mercury was again frozen at E, the tube detached from the Andrews apparatus and re-connected with the filling apparatus. The gas was pumped off and introduced into the point burette K where its volume was measured. The actual method of reading the volumes of liquid and vapour in the experimental tube was that used by Sydney Young.* At each temperature, readings of the liquid and vapour were taken at four different volumes, and from these data the volumes of vapour yielded by a given volume of liquid were calculated.

The constancy of these ratios was taken as a criterion of the purity of the gas and of the accuracy of the measurements. From these ratios and the known volume of gas in the experimental tube the densities of liquid and vapour were afterwards calculated. In determining the orthobaric volumes by this method it is essential that the volume of the experimental tube containing liquid and vapour shall remain constant for a long enough interval to ensure the attainment of equilibrium between the liquid and gaseous phases and between the temperature of the tube and the bath in which it is immersed. In order to obviate slow changes in volume produced by the change of temperature of the mercury in the Andrews apparatus, we adopted the expedient of keeping the mercury in the capillary tube frozen at E during the readings. Since four readings were made at each temperature, this procedure necessitated thawing and re-freezing the mercury each time the volume was changed, but this disadvantage was more than compensated by the increased accuracy of the readings.

Measurements were made at temperatures ranging from 16° to −66° C. Above 0° the tube was immersed in water contained in a silvered Dewar vacuum vessel, and the temperature was adjusted from time to time by the addition of small fragments of ice. The bath was stirred by means of a stream of air which had previously been cooled, and no difficulty was experienced in keeping the temperature constant to within 0·02°.

Below 0° a bath of alcohol cooled by the addition of small pieces of solid carbon dioxide was used. The higher temperatures were read by means of a standard mercury thermometer, and for temperatures below −20° a pentane thermometer graduated in tenths of a degree, which had been compared with a pentane thermometer standardised at the National Physical Laboratory, and kindly lent us by Prof. Trouton, was employed. The difficulty of maintaining the temperature of the bath constant when working below −30° was overcome by stirring with a stream of air cooled by a mixture of solid carbon dioxide and alcohol. The uncertainty of these temperature

* 'Trans. Chem. Soc.,' 1893, vol. 63, p. 1199.

readings did not exceed 0·1° C. The results which are given in the following table refer to two separate fillings of the tube, which yielded, however, for the densities at 0° values falling within the limits of experimental error. The total volume of xenon used measured at normal temperature and pressure 16·79 c.c. and 8·752 c.c. in the two cases. The densities of liquid and vapour are expressed in grammes per cubic centimetre, and are therefore in terms of the density of water at 4°. In calculating the results, corrections were applied for the errors of the thermometers, the variation of the volume of the tube with temperature, and for the forms of the meniscus of liquid and mercury.

Orthobaric Densities of Xenon.

Temperature.	Vapour density.	Liquid density.	Mean density observed.	Liquid and vapour calculated.	$\Delta \times 1000$ obs. — calc.
°	grm. per c.c.	grm. per c.c.			
16	0·844	1·468	1·156	1·156	0
15	0·779	1·528	1·158	1·159	−1
14	0·740	1·592	1·166	1·162	+4
12	0·662	1·677	1·169	1·168	+1
10	0·602	1·750	1·176	1·174	+2
5	0·501	1·879	1·190	1·190	0
0	0·421	1·987	1·204	1·205	−1
−5	0·363	2·074	1·219	1·220	−1
−10	0·313	2·169	1·241	1·236	+5
−20·25	0·235	2·297	1·266	1·267	−1
−30·3	0·180	2·411	1·296	1·298	−2
−39·3	0·139	2·506	1·323	1·325	−2
−49·2	0·103	2·605	1·354	1·355	−1
−59·3	0·078	2·694	1·386	1·386	0
−66·8	0·059	2·763	1·411	1·409	+2

The observed mean densities of liquid and saturated vapour when plotted against the temperature were found to lie very nearly on a straight line. Taking a mean value of all the data, the equation to this straight line is expressed by the formula

$$D_t = 1 \cdot 205 - 0 \cdot 003055t,$$

when D_t is the mean density and t is the temperature in degrees centigrade. Hence, between these limits of temperature, xenon follows Cailletet and Mathias's law of rectilinear diameters.

Critical Temperature and Pressure.—Direct readings of the critical temperature were made on several samples of the gas in the compression apparatus, using the method of Sydney Young. The value finally obtained, and which has been confirmed by later measurements, was 16·6°. This is distinctly higher than the original value of Ramsay and Travers, viz., 14·75°. For the critical pressure, readings were taken on the critical isothermal, and

the pressures observed were plotted on a diagram against the volumes. The point at which the flexure of the curve changes its sign was taken as corresponding to the critical pressure. The value found was 44·27 metres or 58·2 atmospheres.

Critical Volume.—Knowing the critical temperature, the critical density was calculated by means of the equation already cited, on the assumption that the diameter was strictly rectilinear. It proved to be 1·155 grm. per cubic centimetre, corresponding to a critical volume of 0·866 c.c. per gramme. Xenon has therefore a smaller critical volume and a greater critical density than any other substance so far investigated. Immediately above the critical temperature gaseous xenon is heavier than water.

Vapour Pressures.—A few measurements of the vapour pressures of the liquefied gas were made, but the complete vapour pressure curve has not been determined.

Experiments on this point are in progress. The results obtained are :—

Temperature.	Vapour pressure.
°	metres.
10	38 ·702
0	31 ·360
−10	25 ·246
−20	19 ·056

From these data the boiling point of xenon has been calculated by the method of Ramsay and Young. The ratios of the temperatures at which xenon and methyl alcohol have the same vapour pressure were plotted against the corresponding temperatures of methyl alcohol. The four points were found to lie nearly on a straight line, and by extrapolation the value of the ratio at the boiling-point of methyl alcohol was obtained, and the boiling-point of xenon calculated from it. The value found for the boiling-point was −106·9° C., which, like the critical point, is higher than the value −109·1° found by Ramsay and Travers, but on account of the some-what large extrapolation and the small number of points, we regard this figure as only approximately correct.

The mean density at the boiling point of liquefied xenon can be calculated approximately if, as seems probable, the diameter is straight between −66·8° and −106·9°. The value so obtained is 1·538. The density of the saturated vapour, given with sufficient accuracy by assuming the normal coefficient of expansion is 0·013. Hence the liquid density at the boiling point = 1·538 × 2 − 0·013 = 3·063 grm. per cubic centimetre, and the atomic volume of xenon = 130·7/3·063 = 42·7.

Although these values are somewhat different than those calculated by Rudorf for this element, they show that in the argon series there is not only a steady increase in liquid density, but also a progressive rise in atomic volume, with rise in atomic weight, as can be seen in fig. 2.

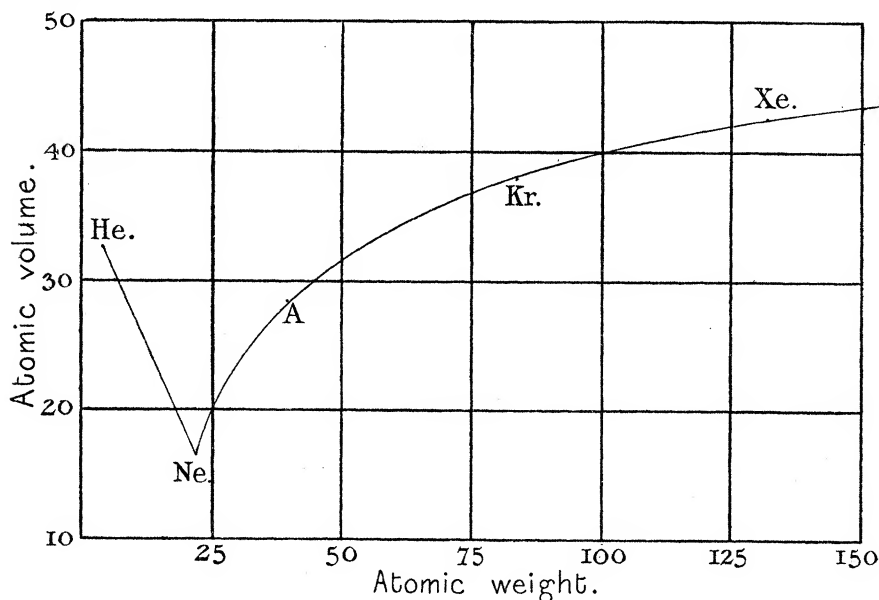A study of the equation of the rectilinear diameter shows that the variation

FIG. 2.

in the mean density of liquid and saturated vapour with change of temperature is for xenon remarkably large. For most substances the angular coefficient lies between -0.0023 and -0.0005.*

Recently, Kamerlingh Onnes and Crommelin have drawn attention to the singularly large coefficient possessed by argon,† viz., -0.003050. The correspondence between this number and our own is striking. The diameters of argon and xenon have not only an almost identical slope, but the slope is greater than that of nearly every substance so far investigated.

The angular coefficient of the helium diameter has been deduced by Onnes from his experiments at very low temperatures on the liquefied gas, and found to be -0.0033, a number not very far removed from that of xenon or argon. A large angular coefficient would appear to be a characteristic of the rectilinear diameters of the rare gases.

Mathias has pointed out‡ that, if van der Waals' law of corresponding

* Mathias, 'Le Point Critique des Corps Purs,' pp. 9 and 10.
† 'Proc. Roy. Acad. Amsterdam,' 1911, vol. 13, p. 1020.
‡ 'Mémoires de la Société Royale des Sciences de Liège,' 1899, 3rd ser., vol. 2.

states were strictly true for the orthobaric densities of liquid and vapour, the expression $-\theta\alpha/\Delta = a$, where θ = critical temperature in degrees abs., Δ = critical density, α = angular coefficient of inclination of the diameter a = constant, should be the same for all substances.

In reality, a is not a constant, but varies for different substances from 0·68 in the case of nitrogen to 1·09 in the case of ethylene.

For argon, Onnes and Crommelin found $a = 0·9027$; our results for xenon give $a = 0·766$; so that, viewed from this standpoint, the inactive gases show no greater regularity than the common gases.

The ratio $RT_k/p_k V_k$ or so-called critical coefficient for xenon, calculated from our data, is 3·605, and is hence considerably greater than the value $8/3 = 2·667$, which is required by van der Waals' equation.[*]

This ratio appears to depend on the weight of the molecule, and also on the critical temperature; for substances of low critical point and small molecular weight the critical coefficient is small, whilst Young found that, for the majority of organic liquids he investigated, the ratio approximated to 3·77. If liquefied xenon does not appreciably differ from the majority of liquids in molecular complexity, one would expect its coefficient to exceed that possessed by other gases of smaller molecular weight, as long as their critical temperatures were not far removed from each other. This is exactly what we find, as the following data show :—

	θ.	$RT_k/p_k V_k$.
	°	
Ethylene	284	3·42
Carbon dioxide	304·3	3·59
*Ethane	305	3·55
Xenon...................	289·6	3·60

* Kuenen and Robson, 'Phil. Mag.,' 1902, vol. 3, p. 622.

For helium and argon, Kamerlingh Onnes has recently found the values

Helium, 3·13;   Argon, 3·283;

whilst for oxygen the value 3·346 was obtained. This constant therefore furnishes no evidence that the elements of the argon series in liquid state are less associated or are simpler in molecular aggregation than any other normal liquids.

Appendix.—The value of these experiments depends mainly on the degree of purity of the xenon, and, before concluding, we wish to draw attention to some curious effects noticed during the research, and which led us at first to

* Kuenen, 'Die Zustandsgleichung,' p. 60.

suspect that the gas was slightly contaminated. The first specimen of xenon with which the densities were determined was purified in the manner described already. The gas, when compressed in the Andrews apparatus below its critical temperature, liquefied completely without measurable rise of pressure, and, on increasing the volume again, a given volume of liquid always yielded the same volume of vapour, provided the temperature remained constant. The xenon behaved, in fact, like a very pure liquid free from uncondensable gas.

Before filling the tube a second time, the gas was passed over heated copper oxide, and then over hot lead chromate, and finally treated with solid caustic potash, with the object of removing possible traces of organic impurities. On liquefaction, unsatisfactory results were obtained, and, when the total space confining the two phases was changed, the volume of vapour yielded by a given volume of liquid was found to vary in different points of the tube.

The xenon was next sparked with oxygen, treated with solid caustic potash, and solidified by cooling to the temperature of liquid air. The oxygen was then removed by pumping, and the gas introduced into the compression tube again. The results obtained were even less satisfactory than before, although no trace of uncondensable gas could be detected. Much time was spent in trying to find an explanation of this behaviour; the experimental tube was re-calibrated, the constant temperature bath was carefully tested, but no source of error could be discovered. The old experimental tube was then replaced by a new carefully calibrated tube, without any change in the results. Experiments were next undertaken to see if the density of xenon at pressures in the neighbourhood of atmospheric was altered by treatment with oxygen. It seemed just possible that a compound between oxygen and the gas might be formed, which at high pressure condensed along with the xenon itself in the experimental tube, and which was the cause of the discrepant results. A large number of experiments were made, with the object of detecting this possible combination, but no convincing evidence of the existence of an oxide was obtained.

The method employed was as follows : A mixture of oxygen and xenon was treated in various ways, viz., sparked at ordinary temperatures, submitted to the silent electric discharge, sparked at a low temperature, etc. The xenon was then solidified by means of liquid air, and the oxygen, which under these conditions remains in the gaseous state, was removed by careful and prolonged evacuation with the Töpler pump. The xenon was finally allowed to gasify, and its density determined in a bulb of about 7 c.c. capacity.

Appended is a short summary of the results we obtained :—

Experiment.		Weight of 1 c.c. of gas at 0° and 760 mm.	
I	Xe and O_2 submitted to silent electric discharge and afterwards cooled to −80°	grm. 0·00564	
II	Xe and O_2 sparked at ordinary temperatures	0·00573	Mean of three results.
III	Large quantity of mixture Xe and O_2 sparked and xenon afterwards fractionated	0·00573 (1st fraction). 0·00567 (8th fraction).	
IV	O_2 liquefied and agitated with solid xenon. Oxygen then pumped off as before	0·00581	
V	Xe and O_2 sparked at −80° in special bulb. Xe solidified, oxygen pumped off and density of remaining gas taken at −80°	0·00597	These results are corrected from −80° C. to 0° C., and hence are not strictly comparable with foregoing.
	Xenon alone subjected to same treatment	0·00592	

Since in these experiments the total volume of gas weighed hardly exceeded 7 c.c. it seemed important to check the method by determining the density of pure xenon in the same apparatus. To obtain the pure gas the xenon was mixed with a small quantity of pure hydrogen obtained from palladium, sparked, dried, condensed, and the hydrogen removed by pumping.

Three density determinations were made, and the values agreed within the limits of experimental error with the value found by Moore :—

Experiment.	Weight of 1 c.c. at 0° and 760 mm.
I	0·00585
II	0·00585
III	0·00586
Mean	0·005854
Moore's value......	0·005842

It is hence apparent that the density of xenon is normal after sparking with hydrogen, but in every case after sparking with oxygen, with the exception of Experiment V, too low a density was obtained. It is to be especially noted that Experiment IV, in which the oxygen was merely liquefied and not sparked with the xenon, yielded a nearly normal result. The low values might be caused by the incomplete removal of oxygen from the mixture, but in nearly all the experiments a considerable proportion of the xenon was allowed to escape after the oxygen had been pumped away and before the density was taken.

It is difficult to believe that the solidified gas after this treatment retained as much as 4 to 5 per cent. of free oxygen. Moreover, Experiment IV demonstrates that the mixed gases can be satisfactorily separated by this treatment if the sparking is omitted. Further, in Experiment III, where the mixture was fractionated after sparking, the eighth fraction was distinctly less dense than the first fraction.

The presence of small quantities of ozone in the gas would also account for the low densities, but the precaution was taken of always passing the gas over mercury after sparking and before it was solidified. Moreover, liquid ozone has a deep blue colour, and small traces would be sufficient to tint the solidified xenon. In all the experiments the solid xenon was perfectly white in colour.

On the other hand, it was repeatedly noticed that when the xenon which had been used for the density measurements was collected through the pump and re-solidified it did not completely re-condense, and small quantities of nearly pure oxygen could be pumped off it. It was never found possible, however, by repeated condensations and evacuation to obtain a gas which behaved normally when compressed in the Andrews apparatus. We frequently re-condensed the gas five times, and finally solidified it in the end of the experimental tube, the Töpler pump being kept in constant operation, without obtaining a satisfactory filling. When, however, xenon which had been sparked with hydrogen underwent the same treatment, the gas on compression gave fairly consistent and normal results, as the following figures for the volume of vapour yielded by unit volume of liquid at 0° show :—

After sparking with oxygen...... 4·66, 4·76, 4·91. Mean, 4·78
       ,,   ,,   hydrogen... 4·58, 4·60, 4·63. Mean, 4·60

It will be noticed that after sparking with oxygen, the greatest variation is 2·7 per cent. of mean value, whilst the variation after sparking with hydrogen is only 0·65 per cent. It is also noticeable that the mean value is different in the two cases. A similar difference was also observed in the critical temperatures of the two specimens of gas. The oxygenated samples became critical at temperatures varying from 16·9° to 17·2°, whilst the pure gas had a constant critical temperature of 16·6°.

We think it must be admitted that the presence of a small quantity of free oxygen in the xenon would not explain the results. The supposition that small amounts of ozone were present seems at first sight more likely, but does not bear examination, for, apart from the reasons given already, it is hard to see how ozone could have escaped decomposition on standing for

days together at high pressure in the presence of mercury in the Andrews apparatus.

On the other hand, if we suppose that an oxide is formed, it is clear that it must be a compound of great instability, and from Experiment V it appears to be more readily formed at low than at high temperature. By sparking at ordinary temperatures, a small percentage of oxide might be produced, which might decompose again fairly rapidly on standing, and by cooling its velocity of decomposition might be greatly diminished as well as its velocity of formation. Since xenon is monatomic, the density of any possible oxide must exceed that of the pure gas, and on this hypothesis the decomposition of the greater part of the oxide during the manipulations involved in a determination would be regarded as the cause of the low densities. It is not improbable, however, that we have here to do with an association of two elements which is essentially physical rather than chemical, and is more allied to absorption or solution than to chemical combination. Such a view is supported by the well-known fact that the inactive gases are slowly absorbed by the electrodes in a Plücker tube when the discharge is passed for a long period, and also by the recent experiments of Claude,* and Ramsay and Collie, who found that on passing a discharge between copper electrodes in an atmosphere of helium and neon, the volatilised metal deposited in the tube contained a large quantity of helium together with a little neon.

Although the experiments just described yielded no definite results they show how oxygen can associate itself with xenon in such a way that the presence of the less condensable gas almost escapes detection. Also these observations showed how the pure gas could be obtained and furnish additional proof of the homogeneity of the xenon employed for the critical constants and orthobaric densities.

* 'Comptes Rendus,' 1911, vol. 153, p. 713.